CHM 3400 – Problem Set 10

Due date: Friday, April 17th, via email, by midnight. NOTE: The final exam will be distributed at 5:00pm on Monday, April 20th, and will be due at 5:00pm on Wednesday, April 22nd. The exam is comprehensive

Do all of the following problems. Show your work.

"Your mother cooked with the precision of a chemist"- Lionel Shriver

1) The work function for rubidium metal is $\Phi = 2.09$ eV (1 eV = 1.602×10^{-19} J).

a) What is the value for λ_0, the critical wavelength, for rubidium metal? Give your final answer in nm.

b) In a photoelectron experiment, rubidium metal is illuminated with monochromatic light of wavelength $\lambda = 400.0$ nm. Will electrons be produced? If your answer is YES, find the maximum kinetic energy for the emitted electrons (in both J and eV), and the maximum speed of an emitted electron (in m/s). Note $m_e = 9.109 \times 10^{-31}$ kg.

2) One of the two visible emission lines in the spectrum of atomic sodium occurs at $\lambda = 589.6$ nm. Find the following:

a) The energy of one photon with wavelength $\lambda = 589.6$ nm, in units of cm^{-1}.

b) The energy of one photon with wavelength $\lambda = 589.6$ nm, in units of J.

c) The energy of one mole of photons with wavelength $\lambda = 589.6$ nm, in units of kJ/mol.

3) The experimental value for the rotational constant for the $^{12}C^{16}O$ molecule is B = 1.9313 cm^{-1}. Based on this, find the following:

a) The energy (in cm^{-1}) and frequency (in GHz, 1 GHz = 10^9 Hz = 10^9 s^{-1}) at which the $J = 3 \rightarrow J = 4$ rotational transition will occur in $^{12}C^{16}O$.

b) The equilibrium bond length (r_e) for a $^{12}C^{16}O$ molecule. Give your final answer in nm. Note the following:

$m(^{12}C) = 12.0000$ amu $\qquad m(^{16}O) = 15.9949$ amu

1 amu = 1.6605×10^{-27} kg

4) The experimental value for the vibrational constant for the $^{12}C^{16}O$ molecule is $\omega_e = 2170.2$ cm^{-1}. Based on this, find the value for k, the force constant, for the $^{12}C^{16}O$ bond. Give your final answer in N/m. Data for the masses of the ^{12}C and ^{16}O atoms are given in the previous problem.

5) For the process

$$CH_4(g) \rightarrow CH_3(g) + H(g) \qquad \Delta H_{rxn} = 438.5 \text{ kJ/mol} \qquad (5.1)$$

What is the longest wavelength of light capable of breaking the C – H bond in methane? Assume that all of the energy for breaking the bond comes from the photon that is absorbed, and that the energy to break the bnd is equal to ΔH_{rxn}.

GENERAL HINT – In most of the above problems you need to pay careful attention to dimensional analysis, so that your answers are in correct units.

Solutions.

1) a) The critical wavelength occurs when $(KE)_{max} = 0$, and so

$$\frac{hc}{\lambda_0} = \Phi \text{ ; and so } \lambda_0 = \frac{hc}{\Phi}$$

So $$\lambda_0 = \frac{(6.626 \times 10^{-34} \text{ J•s})(2.998 \times 10^{8} \text{ m/s})}{(2.09 \text{ eV})(1.602 \times 10^{-19} \text{ J/1 eV})} = 5.933 \times 10^{-7} \text{ m} = 593.3 \text{ nm}$$

b) Since 400.0 nm < 593.3 nm, then YES, photoelectrons will be generated.

$$(KE)_{max} = E(\text{photon}) - \Phi = \frac{hc}{\lambda} - \Phi$$

$$(KE)_{max} = \frac{(6.626 \times 10^{-34} \text{ J•s})(2.998 \times 10^{8} \text{ m/s})}{(400.0 \times 10^{-9} \text{ m})} - (2.09 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV}) = 1.618 \times 10^{-19} \text{ J}$$

In terms of eV, $(KE)_{max} = (1.618 \times 10^{-19} \text{ J})(1 \text{ eV}/1.602 \times 10^{-19} \text{ J}) = 1.01 \text{ eV}$

Finally, since $KE = \frac{mv^2}{2}$ then $v_{max} = [2 (KE)_{max}/m_e]^{1/2}$

So $v_{max} = [\, 2 (1.618 \times 10^{-19} \text{ J})/(9.109 \times 10^{-31} \text{ kg})\,]^{1/2} = 5.96 \times 10^{5} \text{ m/s}$

2) a) $$\tilde{E} = \frac{1}{\lambda} = \frac{1}{(589.6 \text{ nm})(1 \text{ cm}/10^{7} \text{ nm})} = 16960. \text{ cm}^{-1}$$

b) $E = hc\,\tilde{E} = (1.9865 \times 10^{-23} \text{ J/cm}^{-1})(16960. \text{ cm}^{-1}) = 3.369 \times 10^{-19} \text{ J}$

c) For one mole of photons, $E_m = N_A E = (6.022 \times 10^{23} \text{ mol}^{-1})(3.369 \times 10^{-19} \text{ J})$

$= 2.029 \times 10^{5} \text{ J/mol} = 202.9 \text{ kJ/mol}$

3) a) $\Delta\tilde{E} = \tilde{E}(J{=}4) - \tilde{E}(J{=}3) = 4•5•B = 3•4•B = 8B = 8\,(1.9313 \text{ cm}^{-1}) = 15.4504 \text{ cm}^{-1}$

$$\lambda = \frac{1}{\Delta\tilde{E}} = \frac{1}{(15.4504 \text{ cm}^{-1})}\ \frac{1 \text{ m}}{100 \text{ cm}} = 6.472 \times 10^{-4} \text{ m}$$

$$c = \nu\lambda \quad \text{and so} \quad \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8} \text{ m/s}}{6.472 \times 10^{-4} \text{ m}} = 4.632 \times 10^{11} \text{ s}^{-1}$$

$$= 4.632 \times 10^{11} \text{ Hz} \ \frac{1 \text{ GHz}}{10^{9} \text{ Hz}} = 463.2 \text{ GHz}$$

b) $$\mu = \frac{m(^{12}C)\, m(^{16}O)}{m(^{12}C) + m(^{16}O)} = \frac{(12.0000 \text{ amu})(15.9949 \text{ amu})}{(12.0000 + 15.9949)\text{amu}}$$

$$= 6.8562 \text{ amu} \ \frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 1.1385 \times 10^{-26} \text{ kg}$$

Since $B = \dfrac{h}{8\pi^2 c\mu r_e^2}$ and so $r_e^2 = \dfrac{h}{8\pi^2 c\mu B} =$

$$= \frac{(6.626 \times 10^{-34}\ \mathrm{J{\bullet}s})}{8\pi^2\ (2.998 \times 10^8\ \mathrm{m/s})\ (1.1385 \times 10^{-26}\ \mathrm{kg})\ (1.9313\ \mathrm{cm^{-1}})\ (100\ \mathrm{cm/m})}$$

$$r_e^2 = 1.2731 \times 10^{-20}\ \mathrm{m}^2 \qquad r_e = (1.2731 \times 10^{-20}\ \mathrm{m}^2)^{1/2}$$

$$= 1.128 \times 10^{-10}\ \mathrm{m} = 0.1128\ \mathrm{nm}$$

4) $\omega_e = \dfrac{1}{2\pi c}\ (k/\mu)^{1/2}$

If we square both sides, we get $\omega_e^2 = \dfrac{1}{4\pi^2 c^2}\ \dfrac{k}{\mu}$

$$k = 4\pi^2 c^2 \omega_e^2 \mu = 4\pi^2\ (2.998 \times 108\ \mathrm{m/s})^2\ (2170.2\ \mathrm{cm^{-1}})^2\ (100\ \mathrm{cm/m})^2\ (1.1385 \times 10^{-26}\ \mathrm{kg})$$

$$= 1903.\ \mathrm{N/m}$$

Two notes. First, to convert from $\mathrm{cm^{-1}}$ to $\mathrm{m^{-1}}$ multiply 100 cm/m. Second, since we entered everything in MKS units above, we knew that k would have units of N/m (as confirmed by dimensional analysis).

5) $\Delta H_{rxn} = \dfrac{N_A\, hc}{\lambda}$

$$\lambda = \frac{N_A\, hc}{\Delta H_{rxn}} = \frac{(6.022 \times 10^{23}\ \mathrm{mol^{-1}})\ (6.626 \times 10^{-34}\ \mathrm{J{\bullet}s})\ (2.998 \times 10^8\ \mathrm{m/s})}{438.5 \times 10^3\ \mathrm{J/mol}}$$

$$= 2.728 \times 10^{-7}\ \mathrm{m} = 272.8\ \mathrm{nm}$$

The significance of this result is as follows. To photodissociate molecules of CH4, we would have to use light of wavelength $\lambda < 273$ nm. This means that photodissociation will not occur in the troposphere (where light from the sun is $\lambda > 290$ nm), and so other processes must occur to remove methane from the troposphere.